Synthesis of Nanoparticles under Cold-Plasma Conditions

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Pyrene-based nano-spheres were synthesized under RF-plasma conditions in an originally designed plasma reactor. The reactor configuration allows the processing of non-volatile, liquid-phase organic compounds or their solutions in volatile solvents, by atomizing them during their injection into the low-pressure reaction vessel. It has been shown that saturated benzene solution of Pyrene generates under Ar-RF-Plasma environments uniformly sized, hard spherical nano-particles. The structure and the thermal behavior of microspheres were analysed using X-ray photoelectron microscopy (ESCA), FTIR spectroscopy and differential thermal analysis (TG / DTA).

Silver layers, composed of nanoparticles were deposited on formaldehyde-RF-plasma functionalized polyethylene (PE) surfaces by taking advantage of the Tollen's reaction. The presence of aldehyde functionalities and the silver on the modified PE surfaces were evidenced using ESCA, Energy disperse X-ray analysis spectroscopy, SEM, and AFM techniques. High concentration of water-based colloidal (nano-size silver particles) silver solutions were also prepared under Dense Medium Plasma (DMP) plasma environments, and the strong bactericide effect of the silver solutions were evaluated. Applications of nano-particle systems are discussed.

Keywords: nanoparticles, cold plasma, dense medium plasma, silver deposition, colloidal silver, pyrene.

1. Introduction

The size-range of nano-particles is usually considered as 1 to 100 nm. This is the range where atomic and molecular interactions strongly influence the macroscopic properties of materials. It is considered that every property is associated with a critical geometrical scale, and if a nano-scale particle or building blocks of a composite material have dimensions smaller than the critical scale dimensions the fundamental physics of the property start to change.

Novel properties occur in comparison to the bulk characteristics due to the small structure size and short time scale of various processes. These materials, are characterized by high surface areas of the pore or surface structures, which provide mechanisms to achieve molecular recognition capabilities (atom-scale-features generated functionalities), initiation of specific interface chemistries and physical interactions. For applications reasons the porous and non-porous nano-structured materials must be processed into specific forms or shapes, which include films, fibers, spheres and macroscale patterned nano-structures. The control of pore or surface structure at the nanometer scale, can result in enhanced separation processes, catalytic process selectivities, magnetic coupling, hardness, ductility, or optical properties. Possibilities open up on this way for the generation of ultra-sensitive chemical sensors, creation of hydrogen storage media, synthesis of nanostructured magnetic materials etc. [1-10].

Due to the very different behavior of nano-scale materials in comparison to their macroscopic relatives, their interaction with biomolecules and microscopic living entities (e.g. bacteria, viruses) should also be specific. It is known, for instance, that colloidal silver is one of the strongest bactericide. The antimicrobial mechanism of action of silver is not fully understood. However, it has been suggested that tetrasilver tetroxide (Ag_4O_4; a molecular crystal form) is biocidal through an electron release mechanism [11]. The effect of silver on microbes is related to the inactivation of enzymes due to the formation of silver complexes with electron donors containing sulfur, oxygen, nitrogen, such as thiols, carboxylates, amides, imidazols, idols and hydroxyls [12-17].

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Due to the fact that silver is relatively non-toxic for mammalian cells [18], its deposition on prosthetic device surfaces (catheters, heart valves, etc.) would also be an attractive approach for avoiding protein and bacterial attachment (biofilm formation). However, silver does not have too many volatile and stable organometallic compounds, and consequently silver deposition through cold-plasma techniques is limited. The only data related to the deposition of silver form an organometallic derivative under cold plasma conditions, is based on the use of perfluoro-1-methylpropenylsilver as a precursor [19]. Both the stability and the volatility of this compound are not adequate for practical applications, and in addition the compound is very expensive.

In this contribution the synthesis of Pyrene-origin nanospheres, the synthesis of water-based, nano-scale, colloidal silver solutions, and the deposition of silver nano-particles on polyethylene surfaces, under various plasma environments, are presented. The bactericide effect of colloidal silver solutions is evaluated.

2. Experimental
2.1 Materials and Methods
Pyrene (Py; 98%, m.p.: 149-151°C), high purity (99.9%) silver wire, paraformaldehyde (powder, 95%), silver nitrate (99% +), H2O ACS reagent, and KOH were purchased from Aldrich Co. High purity argon, used as inert gas media during the synthesis of colloidal silver, and for the plasma-enhanced decontamination of the reactor was obtained from Liquid Carbonic Co. The relative surface atomic concentrations and the non-equivalent C1s, and O1s linkages of plasma synthesized Pyrene-origin nanospheres and that of the formaldehyde-plasma modified and Ag coated polyethylene (PE) surfaces were carried out using a Perkin Elmer Physical Electronics 0 5400 small area ESCA system (Mg source; 15 kV; 300 W; pass energy: 89.45 eV; angle: 45°). Carbon (C1s), oxygen (O1s) and silver (Ag3d) atomic compositions were evaluated and the nonequivalent positions of carbon linkages were analyzed. In order to correct surface-charge-origin binding energy shifts calibrations were performed based on the well-known C1s peak.

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the chemical linkages of microsphers and the plasma functionalized PE surfaces. An ATI-Mattson, Research Series IR instrument was used, which was provided with a GRASEBY-Special Benchmark Series ATR incopartment P/N 11160 unit. All FTIR evaluations were performed under nitrogen blanket generated from a flow-controlled liquid nitrogen tank. Data were collected in the 600-4000 cm⁻¹ wavenumber region with 250 scans for each sample.

The morphologies of plasma-synthesized microsphere populations, the shapes and morphologies of the deposited silver nano-particles on PE surfaces, and the silver clusters structures composed of nano-scale particles, formed as a result of the evaporation of colloidal silver solutions, were analyzed using Scanning Electron Microscopy (SEM). Images of palladium/gold sputtered substrates were produced using a LEO 982 Field Emission, Digital Scanning Microscope.

The presence of silver atoms on the formaldehyde-plasma exposed PE surfaces and which were subsequently immersed into the AgNO3 solution was also evidenced by Energy Dispersive X-ray spectroscopy (EDS).

The morphologies of silver-coated PE film surfaces were analyzed by atomic force microscopy (Digital Instrument Nanoscope III) AFM (scan rate: 1.9 Hz; sampling number: 512).

Differential Thermal Analysis (Seiko TG/DTA 220; heating rate: 5 degrees/min.; nitrogen atmosphere; temperature range: 25-600°C) technique was used to evaluate the thermal behavior of Pyrene-origin nano-spheres.

Thin silver layers were deposited on plasma-functionalized PE surfaces according to the Tollen’s reaction. The Tollen’s reagent contains the diamminosilver(I) ions, Ag(NH₃)₂⁺, and is prepared by mixing aqueous silver nitrate with aqueous ammonia. These ions will oxidize aldehydes to carboxylate ions according to the following reaction:

\[
\text{RCHO} + 4\text{Ag(NH₃)}₂⁺ + 4\text{H₂O} → \text{R-COO}⁻ + 4\text{Ag}^{0} + 8\text{NH}_₃
\]

Tollen’s reagent gives a negative result with all ketones except \( \alpha \)-hydroxy ketones.

The Tollen’s reagent was prepared according to the following procedure: Two drops of 10% sodium hydroxide was added to 20 ml of 5% silver nitrate solution, then 5% ammonium hydroxide was added with constant stirring until any precipitate of silver oxide was dissolved. The silver deposition was performed by immersing a 9 cm²
The bactericide efficiency of colloidal silver solutions prepared under Dense Medium Plasma (DMP) conditions, were evaluated using the following protocol: Three bacterial strains (Pseudomonas fluorescens, Salmonella typhimurium and Entrobacter agglomerans) were grown overnight in trypticase soy broth (TSB) at room temperature. The next day the strains were transferred to TBS diluted 1:100 in distilled water, and grown overnight at room temperature. Then the strains were pooled and inoculated into water (Aldrich Chemical Co.; 432,007-2 ACS grade). After the plasma treatment, samples were directly plated or diluted in phosphate buffer saline then plated on Trypticase soy agar. The plates were incubated at room temperature for 72 hours. To test the injured bacteria, 0.5 ml of each sample was added to 4.5 ml of TSB and incubated at room temperature.

2.2. Plasma treatments
2.2.1. Synthesis of pyrene-origin nano-spheres

The synthesis of nano-spheres was carried out in an originally designed Pyrex-glass plasma reactor (Figure 1). The reactor is composed of two cylindrically shaped, Pyrex glass parts (5, 16), which are connected through a glass-joint unit (6). The upper part (16) is provided with a removable, stainless steel, disc-shaped top (15), which accommodates the connections for the gas feed system (9, 10, 13, 14), MKS capacitance manometer (11), and the injection system (e.g. syringe with Teflon-tipped plunger provided with needles with syringe push-pull valve) (12). The lower end of the upper part of the reactor has a smaller diameter (D2) and it penetrates deeply into the lower part of the reactor (5). Due to this configuration and owning to the fact that the vacuum system (18, 19, 20) is connected far above the lower end of the cylindrical D2 part of the reactor, the non-volatile particles are accelerated directly toward the substrate (3), while the volatile gas-phase components are evacuated on a U-shaped, secondary route (4). The lower part of the reactor is provided with a double wall configuration (1, 2), which allows the re-circulation of controlled temperature liquid agent and the substantial reduction of thermal energy losses due to the presence of the evacuated outside chamber (1). The plasma state is ignited and sustained using two semi-cylindrical, outside-located, copper electrodes (17), and a 13.5 MHz RF (0-1000 W) power supply (8).

Figure 1. Originally designed Pyrex-glass plasma reactor for nonvolatile liquid processing. 1 - vacuumed glass jacket; 2 - glass chamber for the recirculation of controlled temperature fluid; 3 - flow of non-volatile particles; 4 - gas flow; 5 - Pyrex-glass lower part of the reactor; 6 - glass joint; 7, 17 - external semi-cylindrical copper electrodes; 8 - 13.56 MHz RF power supply; 9, 14 - needle valves; 10, 13 - flow controllers; 11 - MKS pressure gauge; 12 - injection system; 15 - stainless steel cap of the reactor; 16 - Pyrex-glass upper part of the reactor; 18 - liquid nitrogen trap; 19 - valve; 20 - vacuum pump; 21 - substrate; 22 - liquid recirculator (thermostat) system.
Conventional cold-plasma processes are *ab initio* low pressure, gas phase reactions and as a consequence only volatile materials or gases can be used as "plasma-gases" for the synthesis or surface modification of materials. This requirement reduces significantly the application areas of cold-plasma processes; almost all higher molecular weight organic compounds, and organic compounds containing main group elements have, at moderate temperatures, vapor tensions which are far below the vapor tension levels required by cold-plasma systems. The use of higher temperatures, at the same time, require complex thermostated facilities, and can lead to the thermal decomposition of starting materials, which excludes from the beginning the utilization of a large number of compounds in plasma processes.

This reactor configuration permits the plasma-processing of non-volatile liquid-phase materials or their solutions in volatile solvents, by injecting them into an inert or reactive-gas plasma environment. The non-volatile, liquid-phase starting materials are atomized during their injection into the vacuum chamber and interact with the plasma species during their transition through the discharge. The surface tension of the non-volatile liquid compounds subjected to the discharge, the vacuum environment and the plasma parameters (RF-power dissipated to the electrodes, pressure in the reaction chamber, nature of the plasma gas, and residence-time of the particles in the discharge zone) will control not only the extent of the plasma-induced chemical modifications of the starting compounds, but also the geometrical shapes and morphologies of the resulting materials. Because of the surface tension of liquid-phase materials the most probable shape of the resulting products will be spherical, and which is assured by the minimal surface-area/surface-energy condition required by the same volume. The intensity of the plasma process and the resident time of the spherical particles in the discharge zone will control the retention or the loose of the spherical shape of the final products and their physical state (solid or liquid state).

In a typical experiment the plasma reactor having a 2 inch diameter silicon wafer substrate, placed in the lower part of the reactor (Figure 1, item: 21), is evacuated to base pressure, then argon-environment is established in the system and the plasma is ignited at the selected parameters. In the next step, 100 µl of saturated Py solution in benzene is injected in 5 equivalent volumes into the argon discharge. At the end of the reaction the system is evacuated to base-pressure level, washed with argon in several evacuation/re-pressurizing cycles, and then re-pressurized to atmospheric pressure by submitting air into the system. The white powder-like material is removed from the non-plasma-zone of the reactor and stored until analytical evaluations are initiated.

During the plasma synthesis the following plasma parameters were employed: Base pressure: 50 mTorr; argon pressure in the absence of plasma: 100 mTorr; argon pressure in the presence of plasma: 120 mTorr; 13.56 MHz RF-power dissipated to the electrodes: 100 W; pressure increase during the injection of pyrene solution: from 120 mTorr to 450 mTorr; pressure recovery period: 1 minutes. It should be mentioned that each injection has been performed after the injection-induced pressure increase recovered to the 120 mTorr level.

2.2.2. Deposition of silver on PE film surfaces.

Creation of aldehyde functionalities on polymeric chains, by using plasma technique, has not been accomplished until now, to our knowledge. Plasma-enhanced oxidation even of polyolefin surfaces (which do not contain oxygen atoms) usually result in the formation of (C=O), O-C=O or C-O-C functionalities. Polymers prepared by conventional reaction-mechanisms (e.g. polymerization, polycondensation, etc., reactions), and which bear multiple aldehyde functionalities on their chains, are also no too numerous and in addition they are water soluble.

To implant aldehyde functionalities into macromolecular chains by using electrical discharges, one have to generate –CH=O groups in the gas phase. These active species are difficult to be synthesized owning to the fact that the C-H bond is significantly weaker (338 KJ/mol) in comparison to the C-O (594 KJ/mol) or C=O (1076 KJ/mol) bonds and consequently the splitting of hydrogen atoms will be the favored reaction mechanism. In addition, formaldehyde is only available commercially in water solution (the highest concentration is close to 37 %) and this solution used as starting material would introduce also water molecules into the discharge. Higher aldehydes are usually less volatile and generate also hydrocarbon fragments under plasma environments.

As a consequence, in our investigations para-formaldehyde (PF) which is an oligomeric
structure of poly(methylene glycol), is used as the starting component for the generation in the discharge of the \(-\text{CH}=\text{O}\) functionalities. PF is a solid-phase material, which decomposes at relatively elevated temperatures into formaldehyde. Accordingly, a specially designed "monomer" feeder (starting material container) has been designed and developed, which allows the controlled decomposition of PF and the introduction of the resulting formaldehyde at selected pressures and flow rates, into the plasma reactor.

Implantation of aldehyde functionalities into PE film surfaces were carried out in a capacitively coupled (20 cm disc-shaped electrodes with a 3 cm gap between them), 40 kHz stainless steel, cylindrical plasma reactor described earlier [20]. Formaldehyde gas was generated by the thermal decomposition of paraformaldehyde in a specially designed stainless steel container provided with a controlled heating unite, pressure gauge, safety valve and with a needle valve system for the connection of the container to the plasma reactor.

In a typical experiment the reactor having the PE film positioned on the lower, grounded electrode, is evacuated to base pressure and the container having the paraformaldehyde is degassed, then the formaldehyde-supply system (FSS) is isolated from the plasma reactor and heated up to the pre-selected temperature. The formaldehyde work-pressure is created in the reactor in the next step, and the plasma is initiated and sustained for the required treatment period. At the end of the reaction the FSS system is isolated from the discharge chamber, the reactor is evacuated to base pressure level and re-pressurized by using air. Then the plasma-exposed PE film is removed from the reactor and stored until analytical evaluations and silver deposition reactions are started.

The following plasma parameters were used during the plasma-mediated aldehyde group implantation reactions: Base pressure in the absence of plasma: 50 mTorr; formaldehyde pressure in the absence of plasma: 200 mTorr; pressure in the presence of plasma: 400 mTorr; RF power dissipated to the electrodes: 250 W; reaction time: 10 minutes; temperature of the FSS container: 170\(^\circ\)C.

2.2.3. Synthesis of colloidal silver solutions.

Water-based colloidal nano-particle silver solutions were prepared in a redesigned version of DMP reactor (Figure 2) [21, 22].

The reactor is composed of a cylindrical glass chamber (7), provided with two, stainless steel, upper and bottom caps (9, 17), and a cooling jacket (4). The rotating, cylindrical stainless steel, upper electrode (19) is equipped with a quartz jacket for avoiding the penetration of the reaction media to the electrode sustaining central shaft and bearings. The upper electrode has a cylindrically shaped cross-section disc-end, which is terminated in an interchangeable ceramic pin-array (8) holder (23). The lower electrode is hollow, and has also an interchangeable conical-cross-section end-piece, and in addition it is provided with channels (25) for the re-circulation of the reaction media. Both

Figure 2. Redesigned version of dense-medium plasma reactor. 1 - DC power supply; 2 - gases evacuation; 3, 26 - coolant exit and inlet; 4, 7 - glass cylinders; 5 - electrical contact; 6 - coolant; 8 - ceramic pin-array; 9, 17 - caps; 10 - non-rotating electrode; 11 - ground; 12 - gas inlet; 13 - motor; 14 - digital controller; 15, 18 - magnetic coupling system; 16 - liquid inlet; 19 - rotating electrode; 20 - sealed volume; 21 - quartz isolator; 22 - recirculating pump; 23 - pins; 24 - electrical discharges; 25 - recirculated flux; 27 - valve.
the spirally located pin-array and the interchangeable metallic part of the lower electrode are made of pure silver. The distance between the pin-array and the lower electrode can conveniently be modified by a micrometric (thimble) screw-system. The reactor is vacuum-tight (copper gaskets) and the rotation of the upper electrode is assured through a magnetic coupling system (15, 18). The reactor can be operated in a batch-type or continuous-flow-system modes, depending on the specific application. Reactive or inert gases can also be introduced into the reactor during the plasma processes, through the hollow lower electrode. The rotation of the upper electrode is digitally controlled in the range of 0-5,000 rpm. The plasma (multitudes of spark discharges) can be initiated and sustained at atmospheric pressure, using adjustable DC or AC power supplies.

In a typical experiment 200 ml pure water is introduced into the reactor, through which argon gas is bubbled, then the rotation of the upper electrode is started at the selected angular speed, and the plasma is initiated and sustained for the required time. At the end of the reaction the plasma-treated liquid is removed from the system and stored for characterization. The experimental conditions employed during the generation of colloidal silver solution were: Angular speed of the upper electrode: 1000 rpm; DC voltage: 200 V; DC current during the process: 1.0-1.5 A; flow rate argon: 20 sccm; reaction time 1 minute.

3. Results and Discussion

3.1. Synthesis of pyrene-origin nano-spheres:

All ESCA evaluations were performed directly from Si-wafer surfaces. Fig. 3 shows the survey diagram of pyrene-based macromolecular structure (P). It can be observed that in addition to the C1s carbon peak (284.7 eV) oxygen (O1s: 532 eV) and nitrogen (N1s: 401 eV) peaks are also present in the diagram. The relative surface atomic concentration data indicate the existence of a structure mainly built up of carbon-carbon bonds (C: 76.3%, O: 21.8% and N: 1.9%).

The HR diagram of the C1s, non-equivalent carbon functionalities exhibits a tri-modal pattern (Fig. 4). The predominant surface area C=C binding energy peak (284.7 eV) is accompanied by low surface area C=O (286.5 eV) and C=O (288 eV) peaks. The presence of oxygen atoms in the plasma-generated structures might be explained by free radical initiated, ex situ, post plasma surface oxidation reactions developed under open laboratory conditions (OLC). The HR O1s diagram (Fig. 5) also indicate the existence of C-O (532.9 eV) and C-C(O)-C (532.5 eV) functionalities in the plasma synthesized structures.

The presence of N1s peak in the survey diagram might be related to the absorption of nitrogen from air during the handling of P under OLC. It should
be mentioned that the absorption of air-origin-\(O_2\) and \(CO_2\) might also contribute to the relative surface atomic composition.

Data from FTIR analysis of P (transmission mode; KBr pellet; wavenumber range: 600-4000 cm\(^{-1}\); resolution 4.0 cm\(^{-1}\)), indicate the totally attenuated C-H (2800-2900 cm\(^{-1}\)) and -C=C- (1600-1620 cm\(^{-1}\)) vibrations, due probably to the extensive, plasma-induced dehydrogenation and structural reorganization mechanisms (Fig. 6).

Comparative DTA/TG/DTG evaluation of the thermal behavior of Py and P (Fig. 7) show that Py melts at 149°C, which is also the thermal - decomposition - initiation temperature. It can be observed that at 272°C all Py is lost as a result of decomposition and evaporation processes (Fig. 7). The thermal behavior of P is totally different in comparison to that of Py. Even at temperatures as high as 600°C the macromolecular structure generated from P loses only 11%, which indicate the presence of an excellent thermal stability. It also should be noted that the DTA diagram of P does not indicate the existence of melting or evaporation (boiling) processes. It appears that P absorbs around 12% nitrogen in the temperature range of 50-125°C as a result of the heating process. The nitrogen is totally lost at (125-177°C) 177°C, and the degassing mechanism is accompanied by a weight loss, which exceeds with 6% the previously absorbed nitrogen quantity. This, allow us to suggest that P absorbs small amounts of nitrogen (and possibly oxygen and carbon dioxide) even at room temperature. This absorption behavior needs however further investigation.

SEM images show that P is incorporated into a uniformly sized (around 100 nm diameter), and perfectly spherical morphologies (Fig. 8). Spherical clusters can be identified all over the Si wafer surface; however, it should be noted that the whole Si wafer surface is coated with nano-sphere-origin structures, which are incorporated into "quilted"-type layer morphologies (Fig. 9). The development of these layers might be significant for the synthesis of high thermal stability, and low K thin films with applications in microelectronics.
3.2. Deposition of silver on PE film surfaces:

Comparative survey and high resolution ESCA data of PE, formaldehyde-plasma-treated PE and silver coated PE are presented in Figs. 10 - 13. The survey (Fig. 10) and the high resolution C1s (Fig. 11) diagrams of PE show the presence only of C-C linkages (285 eV) and a relative surface carbon atomic concentration of around 95.5 %. A low level (0.4%) oxygen atomic concentration can be related to processing origin oxidation or contamination. The formaldehyde-plasma exposed PE substrate clearly shows a significantly increased surface atomic oxygen concentration (Fig. 10; C = 67.4 % and O = 32.5 %), as it was expected.

The C1s diagram exhibit in addition to the C-C binding energy peak, the presence of a fairly intense C=O (288 eV) and a lower surface area, C-OH and or C-O-C (286.5 eV) binding energy peaks. The high resolution O1s binding energy region exhibits only a fairly symmetrical peak corresponding to the C=O (532.3 eV) functionality.

Figure 9. SEM images of pyrene-based background layer. Magnification ×10³; measured diameter: 82 nm.

Figure 10. Survey ESCA diagram of polyethylene, formaldehyde-plasma treated PE and silver coated PE.

Figure 11. High resolution C1s ESCA peak of untreated polyethylene (U), formaldehyde-plasma treated PE (P) and silver coated PE (Ag).

This substantiates the earliest conclusion that the C=O and/or CH=O groups a predominant in comparison to the C-OH and or C-O-C functionalities. However, additional oxygen was not introduced into the system, which allow us to admit that most of the oxygen-based peaks have an aldehyde structures.

Silver coated PE substrate surfaces clearly indicate the presence of high silver atomic concentrations (Fig. 10; C = 35.5 %; O = 44.3 % and Ag = 20.2 %). The presence of Ag3p½, Ag3p¾, and Ag3d¾ (384.7 eV) and Ag3d½ (368.7 eV) binding energy peaks are obvious both in the survey (Fig. 10) and high-resolution (Fig.
12) diagrams. More than that, the C1s diagram clearly indicate the formation of carboxylate (ions) O-C=O functionalities (289.2 eV) (Fig. 11-Ag) as a result of the reduction of diammonium silver ions and oxidation of aldehyde groups.

The pattern of the high-resolution O1s binding energy zone (Fig. 13) also substantiate the conclusion that carboxylate ion formation is promoted during the silver deposition. The existence of two O1s binding energy peaks (O=C-O*: 533.4 eV and *O=C-O, 532.1 eV) also indicate that the redox reaction took place.

The surface morphology changes of PE generated as a result of formaldehyde-plasma treatment and the silver deposition are evidenced by AFM evaluations (Fig. 14). It can be observed
that the very smooth surface topography of PE films exhibited by both top view and 3D AFM images, are replaced by surfaces containing well-organized nano-particles in the 50-150 nm range. SEM images (Fig. 15) substantiate the AFM findings; the existence of a granular surface structure of the silver-coated PE surfaces is obvious. Energy dispersive X-ray spectroscopy data (Fig. 15; Inserted EDS diagram) prove that the spherical nano-scale particles are made of silver.

3.3. Synthesis of colloidal silver solutions

SEM images of nano-particle silver clusters formed by the evaporation of 100 µl colloidal silver solution (200 ml water; 20 second plasma reaction) clearly indicate the nano-scale nature of the DMP-plasma synthesized particles (Fig. 16).

The bactericide characteristics of plasma-generated colloidal silver solutions are presented in Table 1. It can be observed that extremely short plasma treatment times are enough to kill high concentration bacterial populations. It also can be noted that even very dilute colloidal silver solution (Table 1, line 5) have a significant bactericide effect.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (s)</th>
<th>Plate counts of surviving bacteria (CFU/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial inoculum of water</td>
<td>-</td>
<td>5.73</td>
</tr>
<tr>
<td>2 Water held until treated</td>
<td>-</td>
<td>257,040</td>
</tr>
<tr>
<td>samples were plated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Bacteria sample treated for 5s</td>
<td>5</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>4 Bacteria sample treated for 10s</td>
<td>10</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>5 Bacteria sample treated for 1 min</td>
<td>60</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>6 Water ACS treated and added 1:1 to bacteria sample</td>
<td>60</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>7 1 ml of bacteria sample treated for 10 s added to 200 ml untreated bacteria sample</td>
<td>-</td>
<td>3.69</td>
</tr>
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Table 1. Bacterial inoculum treated in DMP reactor (200 V, 1 A).

Figure 15. SEM images of untreated (left) and silver deposited (right) polyethylene. Magnification: x24000(top); x125000(bottom).
4. Conclusions

It has been demonstrated that organic and inorganic nano-particles can be synthesized using various plasma technologies.

By injecting a saturated benzene-based pyrene solution into an Ar-RF-plasma environment, uniformly sized (100 nm) nano-sphere populations are produced. These structures have high thermal stability and they might find their applications in the area of catalysis.

High concentration of colloidal (nano-scale) silver solutions were prepared under DMP-plasma conditions and tested for bactericide characteristics. It was demonstrated that 10 seconds synthesis of colloidal silver in a bacterial inoculum (number of bacteria: $5\times10^5$ in 150 ml of water) is long enough to kill all bacteria.

Thin silver layers composed of silver nano-particles were deposited on formaldehyde-plasma functionalized PE film surfaces by taking advantage of the Tollen’s reaction. Survey and high resolution ESCA data, energy depressive X-ray spectroscopy, AFM and SEM microscopy prove the presence of nano-particle-based silver layers and the plasma-induced implantation of aldehyde functionalities onto PE film surfaces. Potential applications for the plasma-generated colloidal silver solutions and for the thin silver layers can be envisaged in the fields of disinfections of potable water, creation of antiseptic prosthesis devices, generation of electrically conductive thin layers on dielectric surfaces, etc.

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